



Short communication

High capacity Na–O₂ batteries with carbon nanotube paper as binder-free air cathodeZelang Jian^a, Yong Chen^{a,b}, Fujun Li^{a,c}, Tao Zhang^a, Chang Liu^d, Haoshen Zhou^{a,*}^a Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba 305-8568, Japan^b Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan University, 58 Renmin Road, Haikou 570228, China^c Department of Engineering, The University of Tokyo, Building 5-607, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan^d Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

HIGHLIGHTS

- CNT paper was firstly introduced to Na–O₂ battery.
- The cell showed high capacity and small potential gap.
- Na₂O₂·2H₂O is identified as the main crystalline discharge product.

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ABSTRACT

A carbon nanotube paper without any binders and additives was directly used as the catalyst for Na–O₂ batteries. Corresponding electrochemical performances were investigated. A large discharge capacity can be high up to 7530 mAh g^{−1}, which, to the best of our knowledge, is the highest value obtained at the similar current density. The cycling performance of the Na–O₂ battery can be improved with a capacity limit of 1000 mAh g^{−1}. Moreover, the overpotential gap was as small as 200 mV. Na₂O₂·2H₂O is identified by X-ray diffraction (XRD) as the main crystalline discharge product and can be decomposed in the following charging process as revealed by scanning electron microscope (SEM). These results indicate that the CNT paper is a promising cathode for Na–O₂ battery.

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1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronics and are promising energy storage/conversion devices for hybrid electric vehicles (HEV) and electric vehicles (EV) [1]. However, the energy density of LIBs cannot meet the requirements of long-range running, even the theoretical limited of current electrode materials are reached [2]. Li–O₂ batteries (non-aqueous electrolytes) with a high theoretical energy density of about 3505 Wh kg^{−1}, which is comparable with that of gasoline [3,4], may be a solution to electrifying transportation. The current challenges faced by Li–O₂ batteries that limit their practical application are as follows: 1) the potential gap of Li–O₂ batteries is usually higher than 1 V, which induces a low round-trip efficiency, such as 62% in a pure carbon cathode [5]. Even when a precious

metal is used as an electrochemical catalyst, the round-trip efficiency remains lower than 80% [6], which cannot meet the demands of practical propulsion batteries; 2) Li₂O₂, the desirable discharge product of Li–O₂ batteries, can react with carbon cathode at high voltages, which results into decayed cycling performance; [7] 3) the intermediate discharge product LiO₂ readily attacks the binder poly(vinylidene fluoride) (PVDF) to generate LiF and H₂O₂, which further reacts with Li₂O₂ to form LiOH [8]. New battery systems are necessary to overcome such drawbacks.

Recently, Pascal Hartmann and his coworkers [9] have achieved reversible discharging/charging cycles with a low overpotential of less than 200 mV in a Na–O₂ battery. The round-trip efficiency is greatly improved to higher than 90% [9], which is in contrast with that of Li–O₂ batteries. In particular, the charging voltage plateaus of Na–O₂ batteries are significantly lower than that of Li–O₂ batteries. In such a case, carbon corrosion may not be a problem at low voltages, thereby overcoming the first and second drawbacks in Li–O₂ batteries described above. Binder-free materials are

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expected to solve the third drawback. However, only a few studies have focused on Na–O₂ battery, and thus, more experiments should be conducted to understand the issues in the use of Na–O₂ batteries.

Carbon and carbon-based materials have been intensively studied as catalysts for Li–O₂ batteries [5,10]. Carbon nanotubes (CNTs), which have a large surface area, high electric conductivity, and good corrosion resistance, have attracted significant attention and have shown excellent electrochemical performance [11]. In this study, a CNT paper was prepared via a floating catalyst chemical vapor deposition method. The CNT paper was composed of interpenetrating CNTs to improve the electronic conductivity and to create large void spaces inside it. The CNT paper without any binders and additives was used as the catalyst for Na–O₂ batteries. The binder-free CNT paper can be thinner and more porous, considering the mass of the binder in the conventional electrode film. This is important for the storage of the discharge product NaO₂ or Na₂O₂ and the achievable large specific capacity. The corresponding electrochemical performances were investigated.

2. Experimental

The CNT paper was prepared by using benzene as carbon source, ferrocene as catalyst precursor, and thiophene as growth promoter in a tubular furnace [12,13]. Ferrocene is firstly vaporized at about 185 °C, and carried into the reaction tube furnace by H₂ and pyrolyzed to ultrafine Fe catalyst particles above 400 °C. The reaction temperature was maintained at 1200 °C for 1 h and the CNT paper was obtained after natural cooling.

Powder X-ray diffraction (XRD) was performed to characterize the fresh, discharge and charge products on a Bruker D8 Advanced diffractometer with Cu K α ($\lambda = 1.5406$ Å) radiation. The XRD samples, discharged/charged electrodes were taken out from a coin cell and, washed with diethylene glycol dimethyl ether (DEGDME). The samples were enclosed with a thin transparent Kapton film to prevent their exposure to air during testing. Raman spectra were obtained on a Micro Raman spectrophotometer (Ventuno21, JASCO). The morphologies of pristine, discharge and charge electrodes were performed by field emission scanning electron microscopy (FE-SEM, JEOL 6700F).

The CNT paper without any addition of binder or conductive additives was directly used as a cathode in a Na–O₂ battery assembled in a coin cell (CR2032) with holes. The CNT paper was pressed onto a titanium mesh (100 mesh) which served as a current collector. NaSO₃CF₃/DEGDME or NaTFSI/TEGDME (25 μ l) was employed as electrolyte. The electrochemical measurements were performed on Hokudo Denko Charge/Discharge instruments at 25 °C and in the pure O₂ atmosphere.

3. Results and discussion

The CNT paper has a size of about 55×15 mm², as shown in the inset of Fig. 1a. This size can be adjusted depending on the requirement by tuning the collector. Fig. 1a shows the scanning electron microscopy (SEM) image of the CNT paper with a diameter of about 30 nm and a length of several micrometers. The CNTs are interpenetrated together to form a paper. In addition, some small carbon particles attached on the CNTs are observed. The graphitization degree of the as-prepared CNT paper is investigated via Raman spectroscopy, as presented in Fig. 1b. The two peaks located at 1331 and 1581 cm⁻¹ are assigned to the D and G bands, respectively, which are typical bands of graphitic materials. The G band is a zone center vibration mode of graphite, whereas the D band is related to the defects and disordered carbonaceous solid [14,15]. The relative intensity ratio value (I_G/I_D) is applied to describe the defects of carbon materials. The I_G/I_D value of the CNT paper is *ca.* 3.1, which indicates that the CNT paper has a good structural integrity. The sharp and narrow bands further suggest the high graphitization degree of the CNT paper.

Fig. 2a shows the discharge/charge profiles of the Na–O₂ battery at a current density of 500 mA g⁻¹ (0.1 mA cm⁻²). The cathode is prepared by pressing a CNT paper onto a Ti mesh that functions as a current collector and without the use of any binder and conductive additives. The battery is cycled between 1.8 and 4.2 V (vs. Na⁺/Na, the same below) with 0.5 M NaSO₃CF₃ in diethylene glycol dimethyl ether (NaSO₃CF₃/DEGDME) as the electrolyte. The discharge plateau located at about 2.2 V is very flat. The discharge capacity reached 7530 mAh g⁻¹, which, to the best of our knowledge, is the highest value obtained at the same current density. The charge plateau is about 2.4 V, and the discharge/charge potential gap is only 200 mV. The charge capacity is about 3300 mAh g⁻¹, which results in an initial coulombic efficiency of 43.8%. The achieved reversible charge capacity is also higher than that reported previously at the same current density [9,16,17]. The discharge/charge capacity of the second cycle is about 3100 mAh g⁻¹ and 1300 mAh g⁻¹, respectively. The plateau voltages are similar to those in Hartmann's report, but the capacity is much higher than that reported at a low current density of 300 mA g⁻¹ [9]. In Liu's work, the reversible capacity is about 6000 mAh g⁻¹ at a current density of 300 mA g⁻¹, but the potential gap is very large, even larger than that of Li–O₂ batteries [16], and the capacity is only 1428 mAh g⁻¹ at 500 mA g⁻¹ [16]. In our current study, the discharge/charge potential gap is relatively small and the capacity is very high even at a current density of 500 mA g⁻¹. This result can be attributed to the 3-dimensional (3D) interpenetrating network of the CNT paper, which provides a large void space (see Fig. 1a) to accommodate the discharge product and to facilitate fast electron transport, especially during the charging process. With a limited

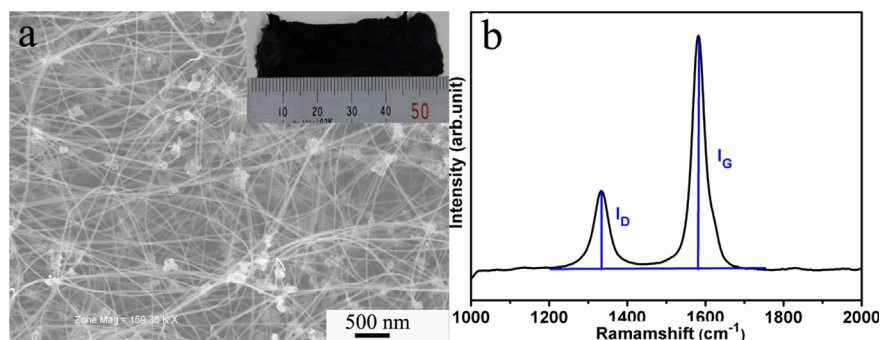


Fig. 1. SEM image (a) and Raman spectrum (b) of a CNT paper. The inset shows an optical image of the CNT paper.

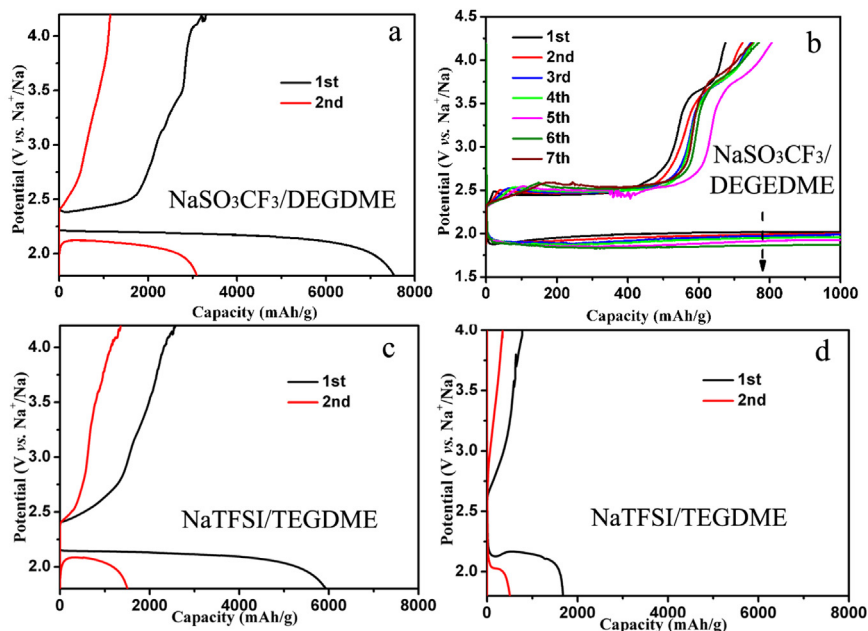


Fig. 2. (a) First two discharge/charge cycles with cut-off potentials from 1.8 to 4.2 V. (b) First seven discharge/charge cycles with a limiting capacity of 1000 mAh g⁻¹ in the 0.5 M NaSO₃CF₃/DEGDME electrolyte with CNT papers as cathodes. First two discharge/charge cycles of Na–O₂ batteries with (c) CNT paper and (d) CNT powder as cathodes, with 0.5 M NaTFSI/TEGDME as electrolyte. The current density is 500 mA g⁻¹.

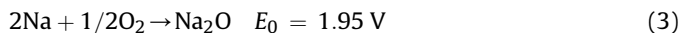
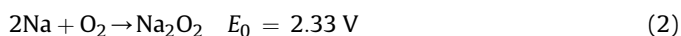
capacity of 1000 mAh g⁻¹ and cut-off potentials from 1.8 to 4.2 V at a current of 500 mA g⁻¹, the discharge/charge curves are illustrated in Fig. 2b. In the first 7 cycles, the discharge capacity is able to reach the limiting value of 1000 mAh g⁻¹, while the reversible charge capacity is about 700 mAh g⁻¹. The observed charge capacity loss indicates the generation of some irreversible discharge products during the discharging process. The discharge and charge voltage plateaus are located at about 2 V and 2.5 V, respectively. The discharge potential decreased with prolonged cycles, as presented in Fig. 2b, which can be attributed to the accumulation of the irreversible discharge product on the CNT paper.

A different electrolyte, 0.5 M sodium bis(trifluoromethanesulfonyl)imide in tetra(ethylene glycol) dimethyl ether (NaTFSI/TEGDME), was also investigated in Na–O₂ batteries with a configuration identical to that of NaSO₃CF₃/DEGDME. The first two charge/discharge cycles are presented in Fig. 2c. The initial discharge and charge capacities are 5930 and 2570 mAh g⁻¹ with a voltage plateau at 2.2 and 2.4 V, respectively. In the second cycle, the discharge and charge capacities decrease to 1500 and 1350 mAh g⁻¹, respectively. The electrochemical performance is similar to the Na–O₂ battery cycled in NaSO₃CF₃/DEGDME. However, the capacity is slightly lower than that of the cell cycled in NaSO₃CF₃/DEGDME electrolyte. The ion conductivity in the NaSO₃CF₃/DEGDME electrolyte is possibly higher than that in the NaTFSI/TEGDME electrolyte. These results indicate that the CNT paper can function as a good air cathode in Na–O₂ batteries with ether-based electrolytes.

A cathode based on CNT powder is comparatively investigated to elucidate further the advantages of the CNT paper for Na–O₂ batteries. The cathode consists of 80 wt% CNT powder and 20 wt% polytetrafluoroethene. At the same current density of 500 mA g⁻¹, the discharge/charge cycles are depicted in Fig. 2d. The discharge voltage plateau is similar, while the charge potential is higher than that in the Na–O₂ battery with a CNT paper cathode, as shown in Fig. 2c. The discharge and charge capacities are very low at only 1680 and 780 mAh g⁻¹ for the first cycle and 505 and 340 mAh g⁻¹ for the second cycle, respectively. The significantly

enhanced electrochemical performance of Na–O₂ batteries with the CNT paper as cathode can be attributed to the following: (1) desirable electrical contact is achieved between the entangled CNTs, and the electrode mass is lower with the absence of a binder; (2) the interpenetrating CNT paper with a 3D configuration can provide both fast electron conduction and large void spaces for the discharge products; and (3) CNTs with high graphitization degree may resist carbon corrosion.

The theoretical voltages of Na–O₂ batteries are listed as follows:



The discharge voltage plateau of our batteries is located at about 2.2 V, which is close to E_0 in the equations (1) and (2). These results indicate that the discharge products are probably NaO₂ or Na₂O₂. In

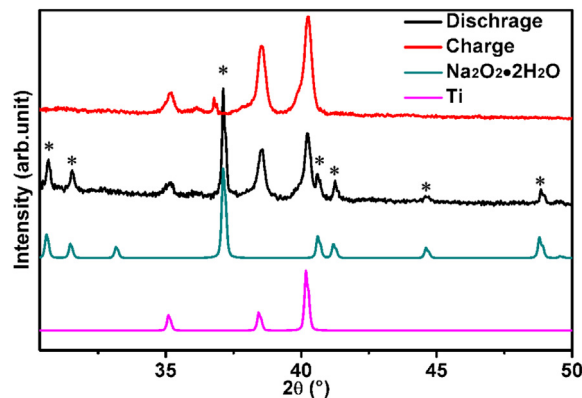


Fig. 3. XRD patterns of the CNT paper cathode after deep discharging and charging.

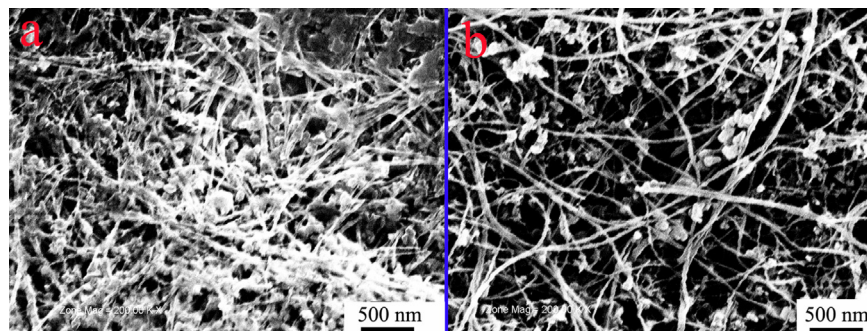


Fig. 4. SEM images of the CNT paper cathode at deep discharged (a) and charged (b) states.

order to clarify the discharge products of Na–O₂ batteries, X-ray diffraction (XRD) measurements were carried out. Fig. 3 shows the XRD patterns of the cathodes in the Na–O₂ batteries with CNT papers as cathodes and 0.5 M NaSO₃CF₃/DEGDME as the electrolyte at deep discharge and charge states. The diffraction peaks of the discharged cathodes are in good agreement with those of Na₂O₂·2H₂O, and no other diffraction peaks can be found, which indicates that the dominant crystalline discharge product is Na₂O₂·2H₂O, which is consistent with the results in the report of Kim [17]. The diffraction peaks of Na₂O₂·2H₂O disappear after charging, that is, the discharge product Na₂O₂·2H₂O is reversibly decomposed. In the oxygen reduction reaction (ORR) process, the sodium metal reacts with O₂ to form NaO₂ or Na₂O₂ and then reacts with H₂O (the decomposed product of ethers as described in the Kim's report [17]) to form Na₂O₂·2H₂O. Further investigation on the mechanism needs.

Fig. 4 shows the SEM images of the CNT paper cathode after deep discharging and charging. Many particles (Na₂O₂·2H₂O) are observed at the discharge state, and their particle size is in the scale of several hundred nanometers, as shown in Fig. 4a. The particles are distributed along the carbon nanotubes occupying the void spaces between the interpenetrating CNTs, which result in the high capacity of the CNT paper. Most of the particles are decomposed when the battery is charged to 4.2 V, as shown in Fig. 4b. The remaining particles may be carbon impurities, as shown in Fig. 1a and (or) undecomposed discharge products, as shown in the charge capacity loss in Fig. 2. The discharge products of Na–O₂ batteries are important for understanding battery reversibility and thus deserve further investigation.

In summary, a 3D interpenetrating CNT paper is employed as a binder-free cathode in Na–O₂ batteries. The CNT paper exhibits the discharge and charge capacities of 7530 and 3300 mAh g^{−1}, respectively, at a current density of 500 mA g^{−1}. The overpotential gap is as small as 200 mV. Na₂O₂·2H₂O is identified as the main crystalline discharge product that can be reversibly decomposed in

ether electrolytes. The reaction mechanism in Na–O₂ batteries and the optimization of electrolytes are undergoing.

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